

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the matter of an application for a German Patent

with the file reference 102 61 545.4

filed on 23 December 2002

in the name of Covion Organic Semiconductors GmbH, Frankfurt am Main,  
Germany,

and in the matter of an application for a United States Patent.

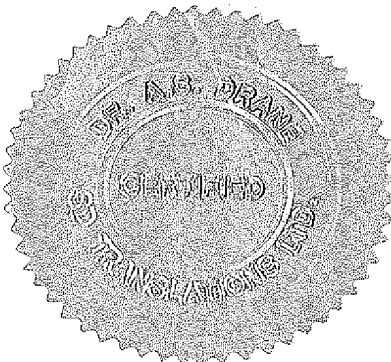
I, Dr. Ashwood Stephen DRANE, B.Sc., Ph.D., BDÜ, translator to SD Translations Ltd. of Beechwood, Chivery, Tring, Hertfordshire, HP23 6LD, England, do solemnly and sincerely declare:

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That I am well acquainted with the German and English languages and am a competent translator thereof.
3. That the following is to the best of my knowledge and belief a true and correct translation of the above-referenced patent application and the Official Certificate attached thereto

Dated this 25th day of March 2008



Dr. Ashwood Stephen Drane



# FEDERAL REPUBLIC OF GERMANY

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## Priority certificate regarding the filing of a patent application

**File reference:** 102 61 545.4

**Date of filing:** 23 December 2002

**Applicant/proprietor:** Covion Organic semiconductors GmbH,  
Frankfurt am Main/DE

**Title:** Organic electroluminescent element

**IPC:** H 01 L, C 07 D, C 09 K

**The attached pages are a correct and accurate reproduction of the  
original documents of this patent application.**

Seal

Munich, 22 October 2003  
**German Patent and Trademark Office**  
On behalf of  
**The President**

[signature]

## Description

## 5 Organic electroluminescent element

The present invention describes a novel design principle for organic electroluminescent elements and to the use thereof in displays based thereon.

10 The use of organic semiconductors as active components (= functional materials) has been reality for some time or is expected in the near future in a number of different applications which can be ascribed to the electronics industry in the broad-est sense.

Thus, light-sensitive organic materials (for example phthalocyanines) and organic-based charge-transport materials (generally triarylamine-based hole transporters) 15 have already been used for many years in photocopiers.

The use of specific semiconducting organic compounds, some of which are also capable of the emission of light in the visible spectral region, is just at the beginning of the market introduction, for example in organic electroluminescent devices. The 20 individual components thereof, the organic light-emitting diodes (OLEDs), have a very broad range of applications as:

1. white or coloured backlights for monochrome or multicoloured display elements (such as, for example, in calculators, mobile telephones and other portable applications),
- 25 2. large-area displays (such as, for example, traffic signs, billboards and other applications),
3. illumination elements in all colours and shapes,
4. monochrome or full-colour passive-matrix displays for portable applications (such as, for example, mobile telephones, PDAs, camcorders and other applications),
- 30 5. full-colour large-area high-resolution active-matrix displays for a very wide variety of applications (such as, for example, mobile telephones, PDAs, laptops, television-s and other applications).

In these applications, the development is in some cases already very well advanced, but there is nevertheless still a great demand for technical improvements.

For relatively simple devices containing OLEDs, the market introduction has already taken place, as confirmed by the car radios with an "organic display" from Pioneer that are available on the market. However, there are still considerable problems which require urgent improvement:

1. Thus, in particular, the OPERATING LIFETIME of OLEDs, in particular for BLUE EMISSION, is still very short, meaning that it has to date only been possible to achieve simple applications commercially. Sanyo has reported lifetimes in the region of about 3000 h for application-relevant brightnesses of blue OLEDs. Materials from Kodak also have similar values.
2. This relative short lifetime gives rise to a secondary problem: in particular for FULL-COLOUR applications ("full-colour-displays"), i.e. displays which do not have segmentation, but instead are able to display all colours over the entire area, it is particularly bad if the colours here age at different rates, as is currently the case. Typical lifetimes for green and red OLEDs are about 30,000 and 20,000 h respectively. This results in a significant shift in the white point occurring even before the end of the above-mentioned lifetime (which is generally defined by a drop to 50% of the initial brightness), i.e. the colour accuracy of the representation in the display becomes very bad. In order to circumvent this, some display users define the lifetime as 70% or 90% lifetime (i.e. drop of the initial brightness to 70% or 90% of the initial value). However, this results in the lifetime becoming even shorter, i.e. entering the region of a few 100 h for BLUE OLEDs.
3. In order to compensate for the drop in brightness, in particular in the blue, the requisite operating current can be increased. However, control of this type is significantly more complex and expensive.
4. Although the efficiencies of OLEDs, especially in the BLUE, are already quite good, improvements are naturally also still desired here – especially for portable applications.
5. Although the colour coordinates of OLEDs, especially in the BLUE, are already quite good, improvements are naturally also still desired here. In particular, the

combination of good colour coordinates with high efficiency must still be improved.

6. The ageing processes are generally accompanied by an increase in voltage. This effect makes a voltage-driven organic electroluminescent devices, for example display or display element, difficult or impossible. However, current-driven addressing is also more complex and expensive in this case.
7. The requisite operating voltage has been reduced in recent years, but must be reduced still further in order to improve the power efficiency. This is of major importance, in particular, for portable applications.
8. The requisite operating current has likewise been reduced in recent years, but must be reduced still further in order to improve the power efficiency. This is particularly important, in particular, for portable applications.

The reasons mentioned above under 1. to 8. make improvements in the production of OLEDs very desirable.

The general structure of organic electroluminescent devices is described, for example, in US 4,539,507 and US 5,151,629.

An organic electroluminescent device usually consists of a plurality of layers, which are preferably applied one on top of the other by means of vacuum methods. These layers are, in detail:

1. A support plate = substrate (usually glass or plastic sheets).
2. A transparent anode (usually indium tin oxide, ITO).
3. A hole-injection layer (= HIL): for example based on copper phthalocyanine (CuPc), conductive polymers, such as polyaniline (PANI) or polythiophene derivatives (such as PEDOT).
4. One or more hole-transport layers (= HTL): usually based on triarylamine derivatives, for example 4,4',4''-tris(N-1-naphthyl)N-phenylamino)triphenylamine (NaphDATA) as the first layer and N,N'-di(naphthalen-1-yl)-N,N'-diphenylbenzidine (NPB) as the second hole-transport layer.
5. An emission layer (= EML): this layer may in some cases coincide with layers 4 or 6, but usually consists of host molecules, for example aluminium tris-8-hydroxyquinoxalinate (AlQ<sub>3</sub>), doped with fluorescent dyes, for example N,N'-

diphenylquinacridones (QA), or phosphorescent dyes, for example tris(phenylpyridyl)iridium (IrPPy).

6. An electron-transport layer (= ETL): in the majority of cases based on aluminium tris-8-hydroxyquinoxalinate (AlQ<sub>3</sub>).

7. An electron-injection layer (= EIL): this layer may in some cases coincide with layer 6 or a small part of the cathode is specially treated or specially deposited.

8. A further electron-injection layer (= EIL): a thin layer consisting of a material having a high dielectric constant, such as, for example, LiF, Li<sub>2</sub>O, BaF<sub>2</sub>, MgO, NaF.

9. A cathode: here generally metals, metal combinations or metal alloys having a low work function, for example Ca, Ba, Mg, Al, In, Mg/Ag, are used.

This entire device is correspondingly (depending on the application) structured, provided with contacts and finally also hermetically sealed since the lifetime of such devices is generally drastically shortened in the presence of water and/or air. The same also applies to inverted structures, in which the light is coupled out of the cathode. In inverted OLEDs, the anode consists, for example, of Al/Ni/NiOx or Al/Pt/PtOx or other metal/metal oxide compounds which have an HOMO greater than 5 eV. The cathode here consists of the same materials described in point 8 and 9, with the difference that the metal, such as, for example, Ca, Ba, Mg, Al, In, etc., is very thin and thus transparent. The layer thickness is below 50 nm, better below 30 nm, still better below 10 nm. A further transparent material, for example ITO (indium tin oxide), IZO (indium zinc oxide), etc., is applied to this transparent cathode.

Organic electroluminescent devices in which the emission layer (EML) consists of more than one substance have already been known for some time:

- EP-A-281381 (Eastman Kodak) describes OLEDs in which the EML consists of a HOST material which is able to transport holes and electrons, and a dopant which is able to emit light. The characteristic feature of this disclosure specification is firstly that the dopant is used in relatively small amounts (generally in the region of about 1%), secondly the HOST material is able to transport (well) holes as well as electrons.

- EP-A-610514 (Idemitsu Kosan) describes OLEDs which have small amounts (< 19%, preferably < 9%) of hole-transporting compounds in the EML. However, only very specific classes of substance are approved here for these compounds. The storage stability of such devices is relatively low.
- EP-A-1162674 (Eastman Kodak) describes OLEDs in which the EML consists of an emitter doped simultaneously with a hole-transporting substance and an electron-transporting substance. It is problematic in a technical respect here that three compounds have to be applied here in a single layer in a very precisely balanced mixing ratio. This is very difficult to achieve industrially with adequate reproducibility, especially in the prevailing process (vacuum vapour deposition).
- EP-A-1167488 (Idemitsu Kosan) describes OLEDs which have a specific combination of anthracene derivatives and aminodistyrylaryl compounds as EML. It is problematic in a technical respect here that the compounds have a very high molecular weight, which results in partial decomposition of the molecules and thus in impairment of application parameters in the prevailing process and at the sublimation temperatures necessary for this purpose.

Surprisingly, it has now been found that OLEDs which conform to the design principle according to the invention – shown below - have significant improvements over the prior art.

The invention therefore relates to an organic electroluminescent device which has at least one emitting layer (EML), where this comprises a mixture of at least one hole-conductor material and at least one emission-capable emission material, and at least one of the two materials contains one or more spiro-9,9'-bifluorene units and the weight ratio of hole-conductor material to emission material is 1 : 99 to 99 : 1, preferably from 5 : 95 to 80 : 20, particularly preferably from 5 : 95 to 25 : 75.

For the purposes of the invention, emission-capable means that the substance, as a pure film in an OLED, exhibits an emission in the range from 380 to 750 nm.

A preferred embodiment of the present invention is an organic electroluminescent device which has at least one emitting layer (EML), where this comprises a mixture

of at least one hole-conductor material and at least one emission-capable emission material, where the HOMO of the hole-conductor material is in the range from 4.8 to 5.8 eV (vs. vacuum), and the compound has at least one substituted or unsubstituted diarylamino group, preferably at least one triarylamino unit or a carbazole group, and the emission-capable emission material contains one or more spiro-9,9'-bifluorene units and the weight ratio of hole-conductor material to emission material is 1 : 99 to 99 : 1, preferably from 5 : 95 to 80 : 20, particularly preferably from 5 : 95 to 25 : 75.

A preferred embodiment of the present invention is an organic electroluminescent device which has at least one emitting layer (EML), where this comprises a mixture of at least one hole-conductor material and at least one emission-capable emission material, where the HOMO of the hole-conductor material is in the range from 4.8 to 5.8 eV (vs. vacuum), and the compound contains one or more spiro-9,9'-bifluorene units and at least one group selected from substituted or unsubstituted diarylamino, carbazole or thiophene units, and the emission-capable emission material is selected from the group of the metal complexes, stilbenamines, stilbenarylenes, condensed aromatic or heteroaromatic systems, but also phosphorescent heavy-metal complexes, rhodamines, coumarins, substituted or unsubstituted aluminium, zinc, gallium hydroxyquinolines, bis(p-diarylamino)arylenes, DPVBi (4,4'-bis(2,2-diphenylvinyl)biphenyl) and analogous compounds, anthracenes, naphthalenes, pentacenes, pyrenes, perylenes, rubrene, QA, benzothiadiazole compounds, DCM (4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran), DCJTb ([2-(1,1-dimethylethyl)-6-[2-(2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H-benzo[*h*]-quinolizin-9-yl)ethenyl]-4H-pyran-4-ylidene]propanedinitrile), iridium, europium, or platinum complexes, and the weight ratio of hole-conductor material to emission material is 1 : 99 to 99 : 1, preferably from 5 : 95 to 80 : 20, particularly preferably from 5 : 95 to 25 : 75.

A preferred embodiment of the present invention is an organic electroluminescent device which has at least one emitting layer (EML), where this comprises a mixture of at least one hole-conductor material and at least one emission-capable emission material, where the HOMO of the hole-conductor material is in the range from 4.8 to



5.8 eV (vs. vacuum), and the compound contains one or more spiro-9,9'-bifluorene units and at least one group selected from substituted or unsubstituted diarylamino, carbazole or thiophene units, and the emission-capable emission material contains at least one spiro-9,9'-bifluorene unit and the weight ratio of hole-conductor material to emission material is 1 : 99 to 99 : 1, preferably from 5 : 95 to 80 : 20, particularly preferably from 5 : 95 to 25 : 75.

The devices described above have the following surprising advantages over the prior art:

1. The OPERATING LIFETIME is increased by a multiple.
2. The efficiency of corresponding devices is higher compared with systems which do not follow the design according to the invention.
3. The colour coordinates are better, i.e. more saturated colours are achieved – especially in the blue region.

Details on the statements made here are given in the examples described below.

Preferred embodiments of the OLEDs according to the invention are those in which the glass-transition temperature  $T_g$  of the respective hole-conductor compound is greater than 90°C, preferably greater than 100°C, particularly preferably greater than 120°C.

A likewise preferred embodiment arises if the glass-transition temperature  $T_g$  of the respective emission compound is greater than 100°C, preferably greater than 120°C, particularly preferably greater than 130°C.

It is particularly preferred if both the described high glass-transition temperature of the hole conductors and also that of the emission materials are present simultaneously.

Due to the high glass-transition temperatures, the preferred embodiments of the devices described here have a further-increased operating lifetime and storage lifetime.

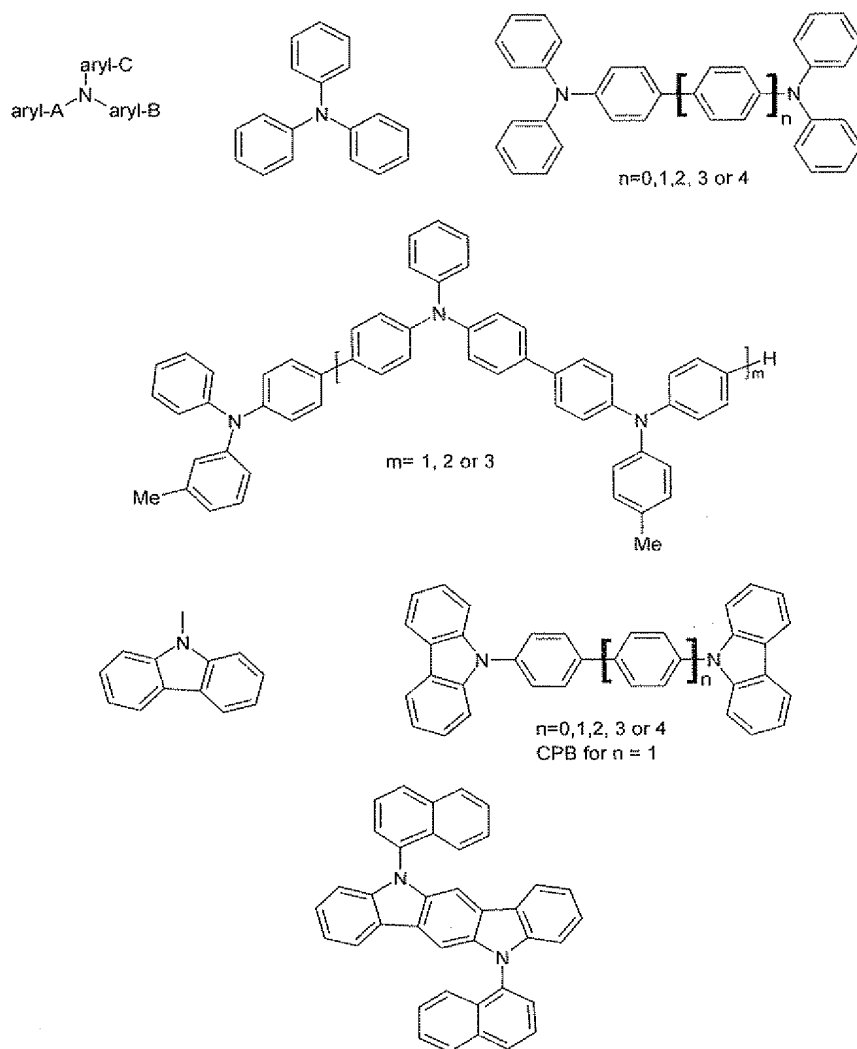
In the OLEDs according to the invention, the layer thickness of the EML is generally selected in the range from 5 to 150 nm, preferably in the range from 10 to 100 nm,

particularly preferably in the range from 15 to 60 nm, very particularly preferably in the range from 20 to 40 nm.

1. The colour coordinates are better, with the optimum layer thickness being obtained for each desired colour, corresponding to the resonance conditions  $d=\lambda/2n$ . For blue-emitting OLEDs, particularly good colour coordinates are obtained if emission layers of 20-40 nm are selected. For green and red OLEDs, the layer thickness must be adapted correspondingly, i.e. increased.
2. The efficiency of corresponding devices is better. The optimum layer thickness ensures a balanced charge balance in the emission layer (emission film) and thus improves the efficiency. In particular, the power efficiency is the greatest in the case of thin emission layers of 20-40 nm.
3. The OPERATING LIFETIME improves by a multiple given an optimum choice of the layer thickness, since a lower current is necessary here with optimum colour coordinates and efficiency.

Preferred hole-conductor compounds are substituted or unsubstituted triarylamine derivatives, such as, for example, triphenylamine derivatives, but also corresponding dimeric or oligomeric compounds, i.e. compounds which contain 2 or more triarylamine sub-units, as sub-group also corresponding carbazole derivatives, biscarbazole derivatives, or also oligocarbazole derivatives, likewise *cis*- or *trans*-indolocarbazole derivatives, furthermore also thiophene, bithiophene and oligothiophene derivatives, likewise pyrrole, bispyrrole and oligopyrrole derivatives; in selected cases, it is also possible for the triarylamino group to be replaced by a hydrazone unit.

Particularly preferred hole-conductor compounds are substituted or unsubstituted compounds of the formulae depicted below:

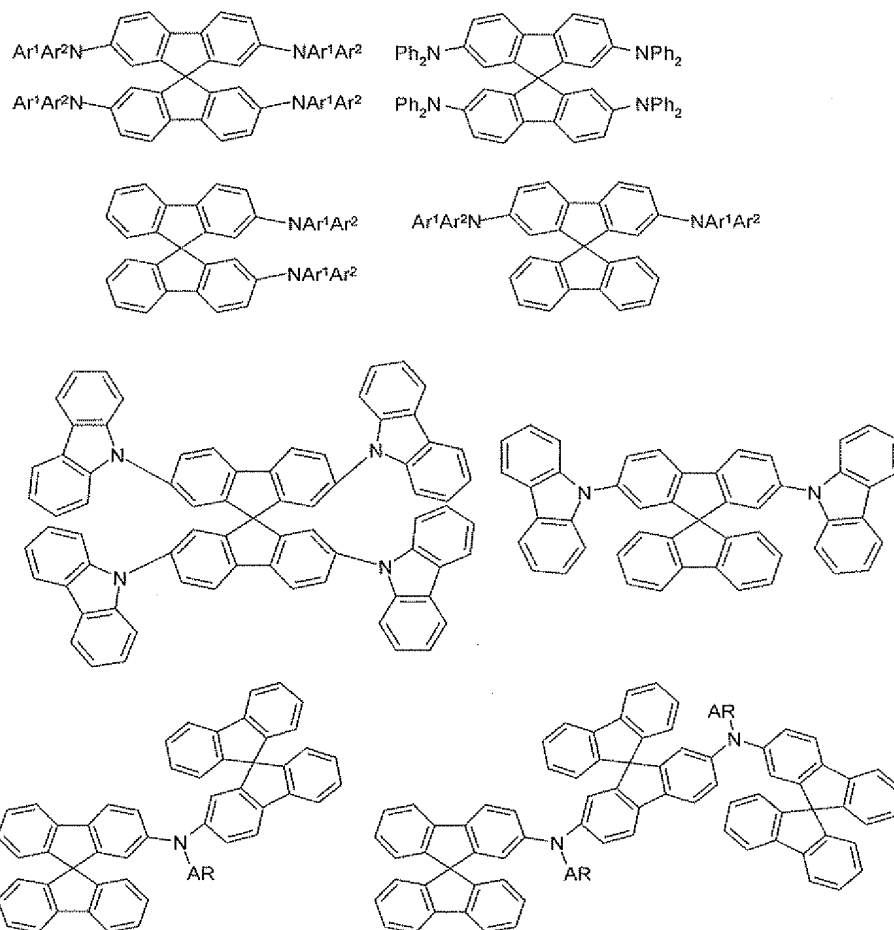


Aryl-A to aryl-C here are intended to stand for aromatic or heteroaromatic rings having 4 to 40 C atoms.

Preferred hole-conductor compounds are spiro-9,9'-bifluorene derivatives which carry 1 to 6 substituents selected from substituted or unsubstituted diarylamino, carbazole, thiophene, bithiophene or oligothiophene group, but also compounds which contain, as substituents or instead of simple aryl groups, one or more substituted or unsubstituted spiro-9,9'-bifluorene derivatives. Preference is given to hole-conductor materials which are in the form of polymers and contain spiro-9,9'-bifluorene derivatives as recurring unit or spiro-9,9'-bifluorene derivatives whose  $M_w$  is a maximum of 10,000 g/mol, particular preference is given to hole-conductor materials

containing spiro-9,9'-bifluorene derivatives and whose  $M_w$  is a maximum of 10,000 g/mol.

Particularly preferred hole-conductor compounds are substituted or unsubstituted compounds of the formulae depicted below:

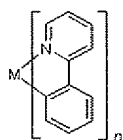


$\text{Ar}^1$ ,  $\text{Ar}^2$  and AR here are intended to stand for aromatic or heteroaromatic rings having 4 to 40 C atoms.

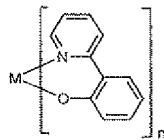
As already mentioned above, preferred emission materials are metal hydroxyquinoline complexes, stilbenamines, stilbenarylenes, condensed aromatic or heteroaromatic systems, but also phosphorescent heavy-metal complexes, rhodamines, coumarins, for example substituted or unsubstituted aluminium, zinc, gallium hydroxyquinolinates, bis(p-diarylaminostryl)arylenes, DPVBi and analogous compounds, anthracenes, naphthacenes, pentacenes, pyrenes, perylenes, rubrene, QA,

benzothiadiazole compounds, DCM, DCJTb, iridium, europium, or platinum complexes.

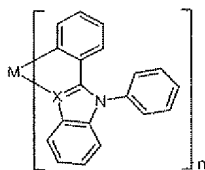
Particularly preferred emission materials are substituted or unsubstituted compounds of the formulae depicted below:



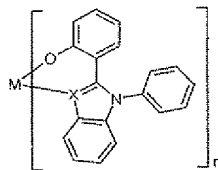
2-(2-phenyl)pyridinato



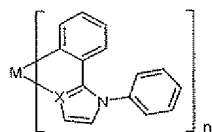
2-(2-hydroxyphenyl)pyridinato



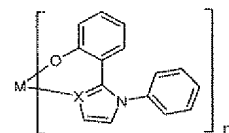
2-(2-phenyl)-1-phenylbenzimid/benzox/benzthi/azolato



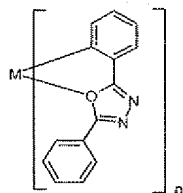
2-(2-hydroxyphenyl)-1-phenylbenzimid/benzox/benzthi/azolato



2-(2-phenyl)-1-phenylimid/ox/thi/azolato



2-(2-hydroxyphenyl)-1-phenylimid/ox/thi/azolato



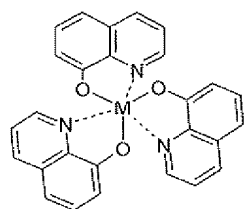
2-(2-phenyl)-5-phenyl-1,3,4-oxadiazolato

in which

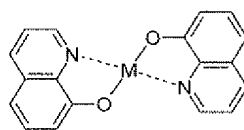
n is identical or different and denotes 1, 2 or 3,

X is identical or different and stands for the elements N, O and S,

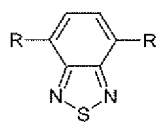
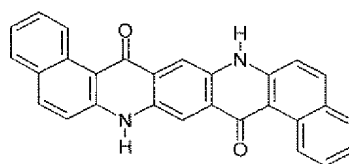
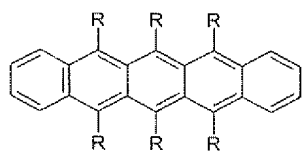
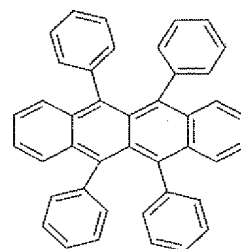
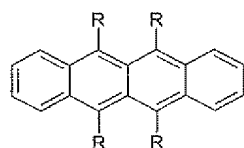
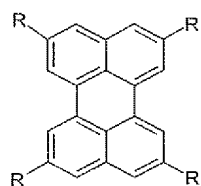
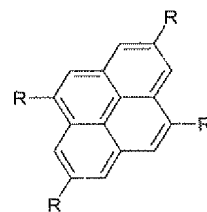
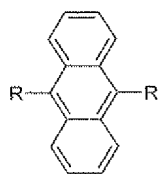
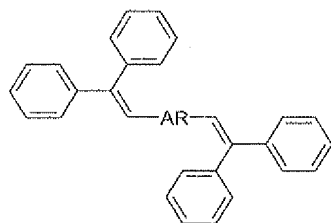
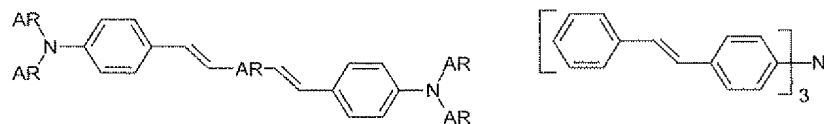
M is identical or different and stands for the elements Li, Al, Ga, In, Sc, Y, La, Cr, Mo, W, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Au, Zn, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

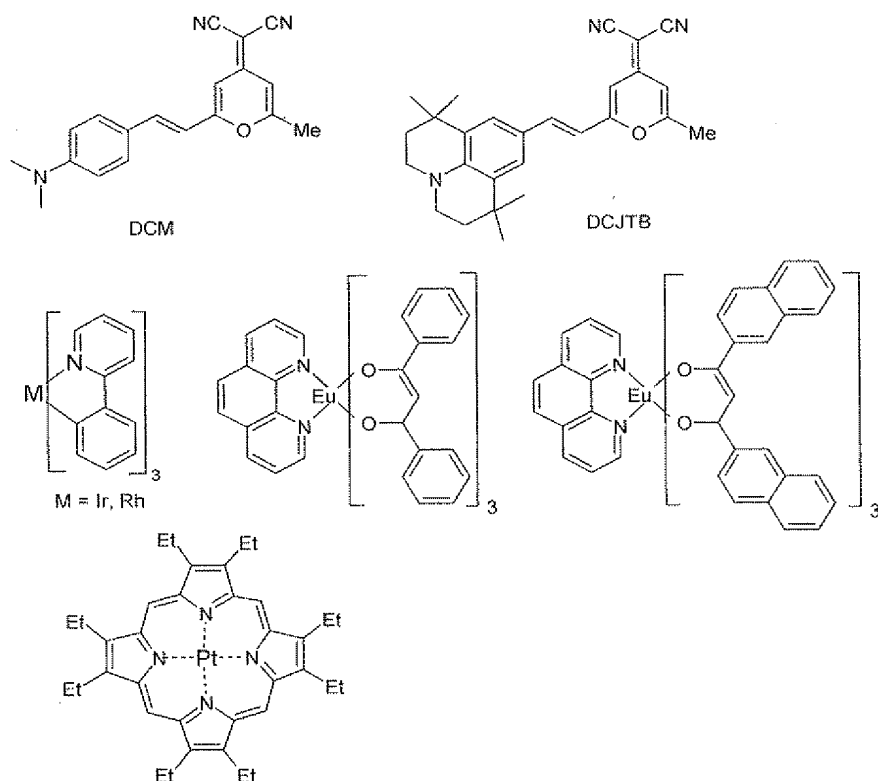


M = Al, Ga



M = Be, Zn





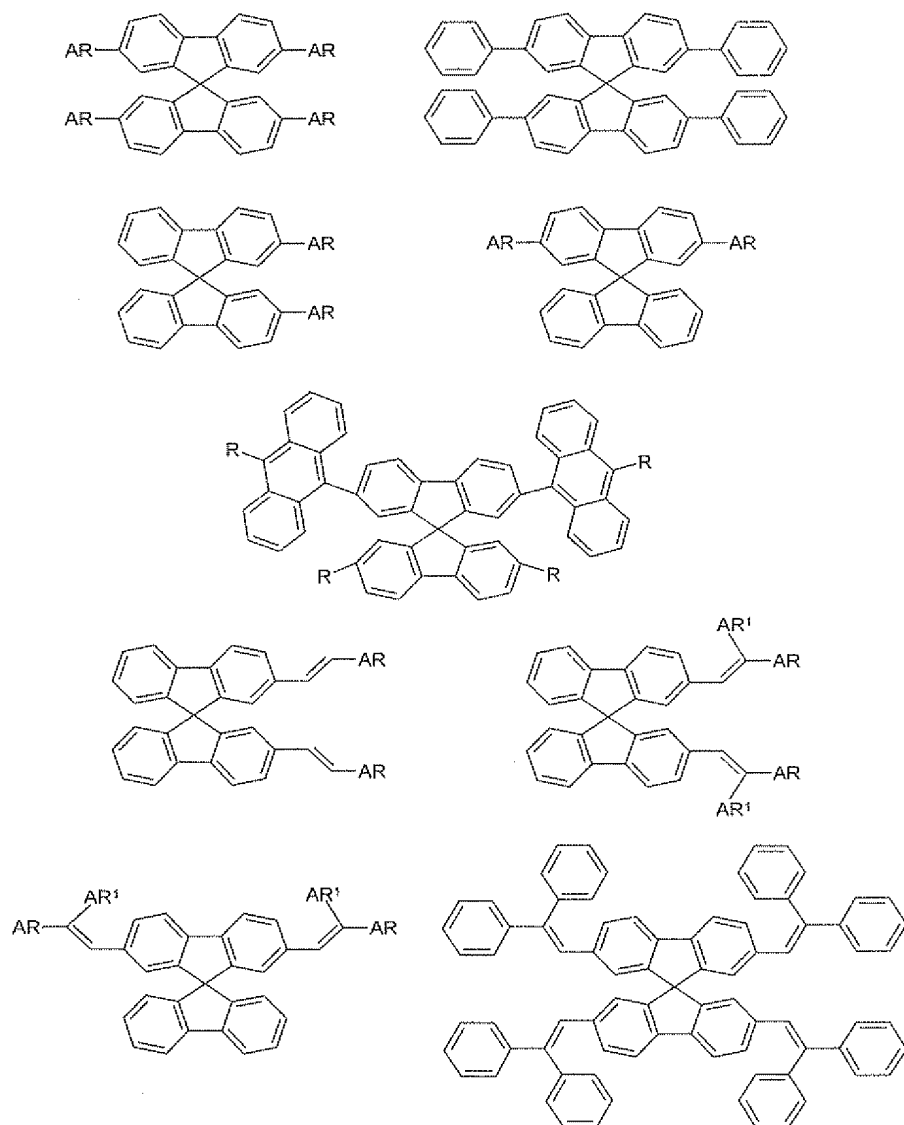
AR here is intended to stand for aromatic or heteroaromatic rings having 4 to 40 C atoms; the substituents R indicate the preferred position of AR groups of this type and should not be regarded as further-restricting here.

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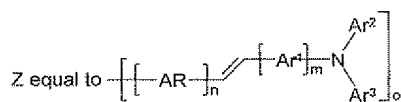
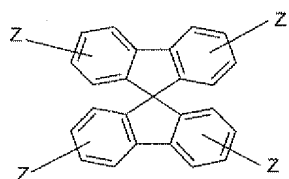
Preferred emission compounds are spiro-9,9'-bifluorene derivatives which carry 1 to 6 substituents selected from substituted or unsubstituted arylenes, heteroarylenes, arylvinylens, diarylvinylens, but also aryls, heteroarylenes, arylvinylens which have one or more substituted or unsubstituted spiro-9,9'-bifluorene derivatives as substituents.

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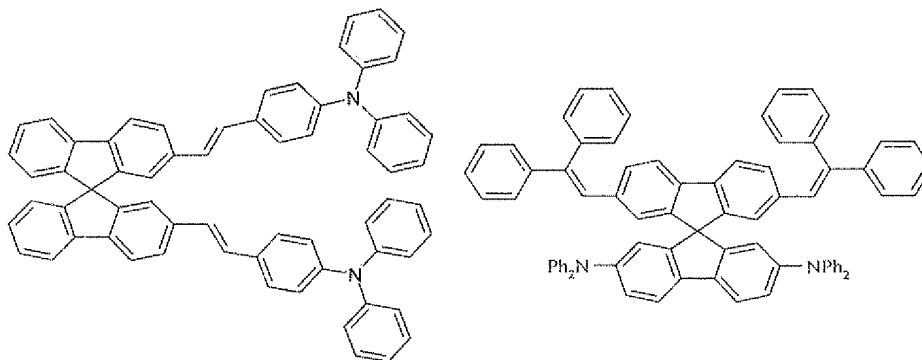
Particularly preferred emission compounds are substituted or unsubstituted compounds of the formulae depicted below:



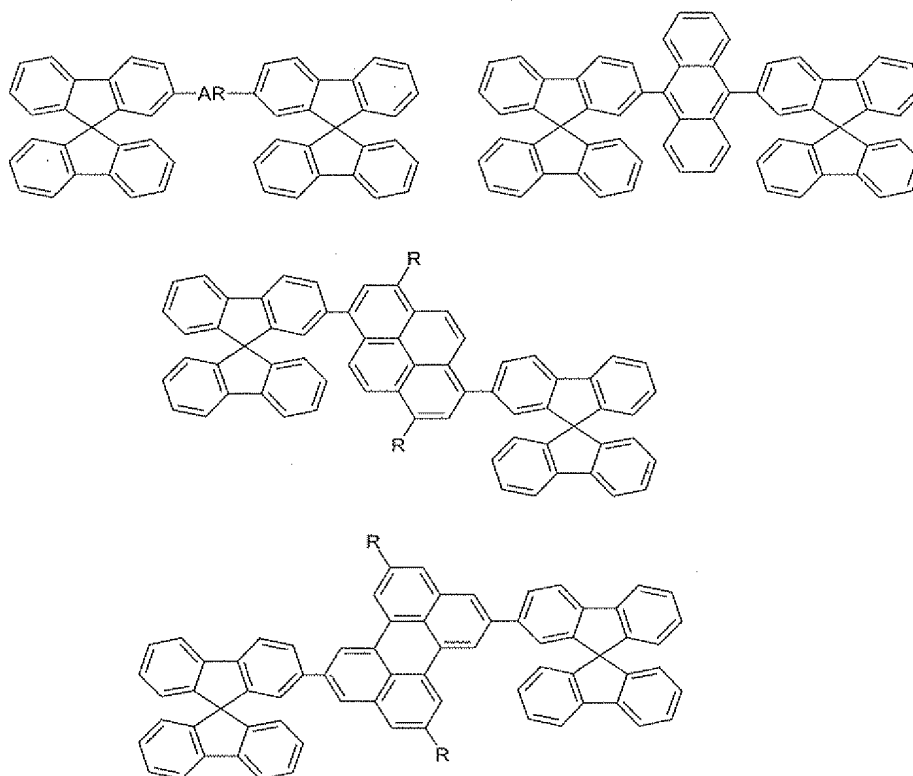




Formula (I)



Formula (II)

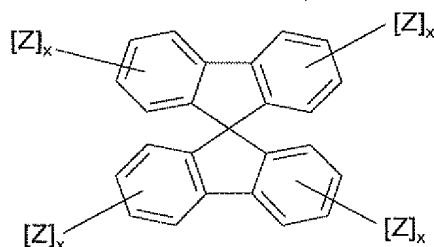


AR, Ar<sup>1</sup>, Ar<sup>2</sup> and Ar<sup>3</sup> here are intended to stand for aromatic or heteroaromatic rings having 4 to 40 C atoms; n corresponds to 0, 1, or 2, m corresponds to 1 or 2, o corresponds to 1, 2, 3, 4, 5 or 6; the substituents R are only intended to indicate a preferred position of groups of this type and should not be regarded as further-

restricting here. The radicals Z in formula I may be present a number of times on an aromatic ring.

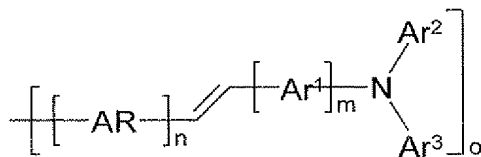
The compounds of the formula (I) are novel.

The invention therefore furthermore relates to compounds of the formula (I)



Formula (I)

in which the radical Z stands for one or more groups of the formula



in which

AR, Ar<sup>1</sup>, Ar<sup>2</sup> and Ar<sup>3</sup> are on each occurrence, identically or differently, aromatic or heteroaromatic rings having 4 to 40 C atoms, which may be substituted by substituents R<sup>1</sup> at the free positions;

n is on each occurrence, identically or differently, 0, 1, or 2;

m is on each occurrence, identically or differently, 1 or 2;

o is on each occurrence, identically or differently, 1, 2, 3, 4, 5 or 6;

x is on each occurrence, identically or differently, 0, 1, 2, 3 or 4, with the proviso that the sum of all indices x is not equal to zero,

R<sup>1</sup> is on each occurrence, identically or differently, a straight-chain, branched or cyclic alkyl or alkoxy chain having 1 to 22 C atoms, in which, in addition, one or more non-adjacent C atoms may be replaced by N-R<sup>2</sup>, O, S, -CO-O-, O-CO-O-, where, in addition, one or more H atoms may be replaced by

fluorine, an aryl or aryloxy group having 5 to 40 C atoms, in which, in addition, one or more C atoms may be replaced by O, S or N, which may also be substituted by one or more non-aromatic radicals  $R^1$ , or Cl, F, CN,  $N(R^2)_2$ ,  $B(R^2)_2$ , where, in addition, two or more radicals  $R^1$  may form a ring system with one another;

$R^2$

is on each occurrence, identically or differently, H, a straight-chain, branched or cyclic alkyl chain having 1 to 22 C atoms, in which, in addition, one or more non-adjacent C atoms may be replaced by O, S, -CO-O-, O-CO-O-, where, in addition, one or more H atoms may be replaced by fluorine, an aryl group having 5 to 40 C atoms, in which, in addition, one or more C atoms may be replaced by O, S or N, which may also be substituted by one or more non-aromatic radicals  $R^1$ .

Electroluminescent devices according to the invention can be produced, for example, as follows:

1. ITO-coated substrate: the substrate used is preferably ITO-coated glass with the lowest possible or no ionic impurities, such as, for example, flat glass from Merck-Balzers or Akaii. However, it is also possible to use other ITO-coated transparent substrates, such as, for example, flexible plastic films or laminates. The ITO must combine the highest possible conductivity with high transparency. ITO layer thicknesses between 50 and 200 nm have proven particularly suitable. The ITO coating must be as flat as possible, preferably having a roughness below 2 nm. The substrates are firstly pre-cleaned with 4% Dekonex in deionised water. The ITO-coated substrate is then either treated for at least 10 minutes with ozone or for a few minutes with oxygen plasma or irradiated for a short time with an excimer lamp.
2. Hole-injection layer (= HIL): the HIL used is either a polymer or a low-molecular-weight substance. The polymers polyaniline (PANI) or polythiophene (PEDOT) and derivatives thereof are particularly suitable. These are usually 1 to 5% aqueous dispersions, which are applied to the ITO substrate in thin layers with a layer thickness between 20 and 200 nm, preferably between 40 and 150 nm, by spin

coating, ink-jet printing or other coating methods. The PEDOT- or PANI-coated ITO substrates are then dried. A plurality of methods are suitable for the drying. The films are usually dried for 1 to 10 minutes in a drying oven between 110 and 200°C preferably between 150 and 180°C. However, more recent drying methods, such as, for example, irradiation with IR (infrared) light, also give very good results, with the irradiation duration lasting only a few seconds. The low-molecular-weight material used is preferably thin layers between 5 and 30 nm of copper phthalocyanine (CuPc). CuPc is usually vapour-deposited in vacuum sublimation units at a pressure below  $10^{-5}$  mbar, preferably below  $10^{-6}$  mbar, particularly preferably below  $10^{-7}$  mbar. However, more recent methods, such as OPVD (organic physical vapour deposition) or LITI (light induced thermal imaging), are also suitable for the coating of low-molecular-weight materials. All HILs must not only inject holes very well, but also adhere very well to ITO and glass; this is the case both for CuPc and also for PEDOT and PANI. Particularly low absorption in the visible region and thus high transparency are exhibited by PEDOT and PANI, which is a further necessary property for the HIL.

3. One or more hole-transport layers (= HTL): in most OLEDs, one or more HTLs are the prerequisite for good efficiency and high stability. Very good results are achieved with a combination of two layers, for example consisting of triaryl-amines, such as MTDATA (4,4',4''-tris(N-3-methylphenyl)-N-phenylamino)-triphenylamines) or NaphDATA (4,4',4''-tris(N-1-naphthyl)-N-phenylamino)-triphenylamines) as the first HTL and NPB (N,N'-di(naphthalen-1-yl)-N,N'-diphenylbenzidine) or spiro-TAD (tetrakis-2,2',7,7'-diphenylaminospiro-9'9'-bifluorene) as the second HTL. MTDATA or NaphDATA cause an increase in the efficiency in most OLEDs by about 20 – 40%; owing to the higher glass-transition temperature  $T_g$ , NaphData ( $T_g = 130^\circ\text{C}$ ) is preferred to MTDATA ( $T_g = 100^\circ\text{C}$ ). The second layer is preferably spiro-TAD ( $T_g = 130^\circ\text{C}$ ) owing to the higher  $T_g$  compared with NPB ( $T_g = 95^\circ\text{C}$ ). Better efficiencies are furthermore achieved for blue OLEDs with spiro-TAD. MTDATA and NaphDATA have a layer thickness of between 5 and 100 nm, preferably 10 and 60 nm, particularly preferably between 15 and 40 nm. For thicker layers, somewhat higher voltages are required in order to achieve the same brightness; at the same time, the number of defects drops. Spiro-TAD and NPB have a layer thickness of between 5 and 150 nm, preferably

10 and 100 nm, particularly preferably between 20 and 60 nm. With increasing layer thickness of NPB and most other triarylaminines, higher voltages are required for the same brightnesses. The layer thickness of spiro-TAD has, however, only a slight influence on the current/voltage/electroluminescence characteristic lines, i.e. the requisite voltage in order to achieve a certain brightness is only slightly dependent on the spiro-TAD layer thickness. All materials are vapour-deposited in vacuum sublimation units at a pressure below  $10^{-5}$  mbar, preferably below  $10^{-6}$  mbar, particularly preferably below  $10^{-7}$  mbar. The vapour-deposition rates can be between 0.01 and 10 nm/s, preferably 0.1 and 1 nm/s. The same applies to the HTL as to the HIL; more recent methods, such as OPVD (organic physical vapour deposition) or LITI (light induced thermal imaging), are suitable for the coating of low-molecular-weight materials.

4. **Emission layer** (= EML): this layer may in some cases coincide with layers 3 and/or 5. It consists, for example, of a host material and simultaneous fluorescent dye, such as spiro-DPVBi (2,2',7,7'-tetrakis(2,2-diphenylvinyl)spiro-9,9'-bifluorene), and a hole-transport material, such as, for example, spiro-TAD. Good results are achieved at a concentration of 5 – 10% of spiro-TAD in spiro-DPVBi with an EML layer thickness of 15 – 70 nm preferably 20-50 nm. All materials are vapour-deposited in vacuum sublimation units at a pressure below  $10^{-5}$  mbar, preferably below  $10^{-6}$  mbar, particularly preferably below  $10^{-7}$  mbar. The vapour-deposition rates can be between 0.01 and 10 nm/s, preferably 0.1 and 1 nm/s. The same applies to the EML as to the HIL and HTL; more recent methods, such as OPVD or LITI, are suitable for the coating of low-molecular-weight materials. For doped layers, OPVP has particularly great potential since the setting of any desired mixing ratios succeeds particularly well. The concentrations of the dopants can likewise be changed continuously. The prerequisite for the improvement of the electroluminescent device are thus optimal in the case of OPVD.
5. An electron-transport and **hole-blocking layer** (= HBL): in particular, BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline = bathocuproin) has proven to be very effective as HBL material. A thin layer of 3 – 20 nm, preferably 5 – 10 nm, increases the efficiency very effectively. All materials are vapour-deposited in vacuum sublimation units at a pressure below  $10^{-5}$  mbar, preferably below  $10^{-6}$  mbar,

particularly preferably below  $10^{-7}$  mbar. The vapour-deposition rates can be between 0.01 and 10 nm/s, preferably 0.1 and 1 nm/s. OPVD is, inter alia, a further method for applying these materials to a substrate.

6. Electron-transport layer (= ETL): highly suitable ETL materials are metal hydroxyquinolates; aluminium tris-8-hydroxyquinolate ( $\text{AlQ}_3$ ), in particular, has proven to be one of the most stable electron conductors. All materials are vapour-deposited in vacuum sublimation units at a pressure below  $10^{-5}$  mbar, preferably below  $10^{-6}$  mbar, particularly preferably below  $10^{-7}$  mbar. The vapour-deposition rates can be between 0.01 and 10 nm/s, preferably 0.1 and 1 nm/s. The same applies to the EML as to the HIL and HTL; more recent methods, such as OPVD or LITI, are suitable for the coating of low-molecular-weight materials.
7. Electron-injection layer (= EIL): a thin layer having a layer thickness of between 0.2 and 8 nm, preferably 0.5 – 5 nm, consisting of a material having a high dielectric constant, in particular inorganic fluorides and oxides, such as, for example,  $\text{LiF}$ ,  $\text{Li}_2\text{O}$ ,  $\text{BaF}_2$ ,  $\text{MgO}$ ,  $\text{NaF}$ , and further materials has proven to be particularly good as EIL. Especially in combination with Al, this additional layer results in a significant improvement in electron injection, and thus in improved results regarding lifetime, quantum efficiency and power efficiency. All materials are vapour-deposited in vacuum sublimation units at a pressure below  $10^{-5}$  mbar, preferably below  $10^{-6}$  mbar, particularly preferably below  $10^{-7}$  mbar. The vapour-deposition rates can be between 0.01 and 1 nm/s, preferably 0.1 and 0.5 nm/s.
8. Cathode: use is generally made here of metals, metal combinations or metal alloys having a low work function, for example Ca, Ba, Cs, K, Na, Mg, Al, In, Mg/Ag. All materials are vapour-deposited in vacuum sublimation units at a pressure below  $10^{-5}$  mbar, preferably below  $10^{-6}$  mbar, particularly preferably below  $10^{-7}$  mbar. The vapour-deposition rates can be between 0.01 and 1 nm/s, preferably 0.1 and 0.5 nm/s.
9. Encapsulation: effective encapsulation of the organic layers including the EIL and the cathode is vital for organic electroluminescent devices. If the organic display is constructed on a glass substrate, there are a number of possibilities. One possibility is adhesive bonding of the entire structure to a second glass or metal plate. Two-component or UV-curing epoxy resins have proven particularly suitable here. The electroluminescent device can be bonded completely here or only

at the edge. If the organic display is only bonded at the edge, the durability can be additionally improved by adding a so-called getter. This getter consists of a very hygroscopic material, in particular metal oxides, such as, for example, BaO, CaO, etc., which binds ingressing water and water vapours. Additional binding of oxygen is achieved with getter materials, such as, for example, Ca, Ba, etc. In the case of flexible substrates, a high diffusion barrier, in particular, should be ensured. In particular, laminates comprising alternating thin plastic and inorganic layers (for example  $\text{SiO}_x$  or  $\text{SiN}_x$ ) have proven successful here.

10. Range of applications: the structure described under points 1 – 9 is suitable both for monochrome and also for full-colour passively or actively operated matrix displays for portable equipment, such as, for example, mobile telephones, PDAs, camcorders and other applications. In the case of passive-matrix displays, 1000 to several 100,000  $\text{cd/m}^2$  peak brightness is required, depending on the number of pixels; initial applications are between 5000 and 20,000  $\text{cd/m}^2$  peak brightness. For full-colour large-area high-resolution displays, active-matrix control is preferred. The requisite brightness of the individual pixels is between 50 and 1000  $\text{cd/m}^2$  preferably between 100 and 300  $\text{cd/m}^2$ . The structure described under points 1 – 9 is also suitable for this purpose. Active-matrix control is suitable for all display applications (such as, for example, mobile telephones, PDAs and other applications), but in particular also for large-area applications, such as, for example, in laptops and televisions. Further applications are white or coloured backlights for monochrome or multicoloured display elements (such as, for example, in calculators, mobile telephones and other portable applications), large-area displays (such as, for example, traffic signs, billboards and other applications), illumination elements in all colours and shapes.

As described above, the devices according to the invention can also be produced by special printing processes (such as the said LITI). This has both advantages regarding scalability of manufacture, and also regarding the setting of mixing ratios in blend layers used.

However, it is very generally necessary for this purpose to prepare corresponding layers (for LITI: transfer layers), which are only then transferred to the actual substrate.

In these layers, compounds A or A' and B or B' are then generally present in the desired ratio (with the exception of any requisite auxiliaries which are necessary for the transfer step).

The present inventions also relate to these layers.

5 The present invention thus furthermore relates to layers which comprise mixtures of compounds A or A' with compounds B or B', and to the use thereof for the production of devices according to the invention.

10 The present application text and also the examples below are directed only to organic light-emitting diodes and the corresponding displays. In spite of this restriction of the description, it is possible for the person skilled in the art, without further inventive step, to produce and apply corresponding layers according to the invention, for example for organic solar cells (O-SCs), organic field-effect transistors (O-FETs) or also organic laser diodes (O-lasers), to mention but a few further  
15 applications.

The present invention is explained in greater detail by the following examples, without wishing it to be restricted thereto. The person skilled in the art will be able to produce further devices according to the invention from the description and the  
20 examples mentioned without inventive step.

The examples enumerated below had the following layer structure:  
glass / ITO (80 nm) / HIL (60 nm) / HTL-1 (20 nm) / HTL-2 (20 nm) / EML (20 – 40 nm) / ETL (10 – 20 nm) / metal-1 (5 nm) / metal-2 (150 nm). Examples 10 and 11  
25 additionally comprised a blocking layer for holes (HBL) between EML and ETL. This gave rise to the following layer structure for this purpose: glass / ITO (80 nm) / HIL (60 nm) / HTL-1 (20 nm) / HTL-2 (20 nm) / EML (20 – 40 nm) / HBL (5 – 10 nm) / ETL (10 – 20 nm) / metal-1 (5 – 10 nm) / metal-2 (150 nm).

- Glass coated with 80 nm of ITO was purchased from Merck-Balzers.
- 30 • The HIL used was a PANI layer having a thickness of 60 nm from Covion (Pat 010) or a PEDOT layer with a thickness of 60 nm from Bayer (Baytron P 4083). The PANI layer was produced from a 4% dispersion by spin coating at 4000 rpm. The resultant layer was conditioned at 180°C for five minutes. The PEDOT layer



was produced from a 2% dispersion by spin coating at 3000 rpm. The resultant layer was conditioned at 110°C for five minutes.

- The HTL-1 used was NaphDATA from Syntec. This material was purified by sublimation before use in OLEDs.
- The HTL-2 used was spiro-TAD from Covion.
- The EML is described in greater detail in Examples 1-13.
- The HBL used was BCP from ABCR. This material was purified by sublimation before use in OLEDs.
- The ETL used was Alq from Covion.
- The metal-1 used was Ba from Aldrich.
- The metal-2 used was Ag from Aldrich.

The organic materials (HTL-1 / HTL-2 / EML / (HBL) / ETL) were vapour-deposited successively at a pressure  $< 10^{-6}$  mbar in a Pfeiffer-Vakuum vapour-deposition apparatus rebuilt by Covion. The unit was fitted with automatic rate and layer-thickness control. The unmixed EML layers, which were produced as reference, were vapour-deposited in the same way as HTL-1, HTL-2, ETL and HBL at a pressure  $< 10^{-6}$  mbar in the Pfeiffer vapour-deposition apparatus. In the case of the mixed EML layers (mixtures of two different materials), two materials were vapour-deposited simultaneously. The concentrations described in the examples were reached by setting the rates in accordance with the mixing ratios. The metals (metal-1 / metal-2) were vapour-deposited at a pressure  $< 10^{-6}$  mbar in a Balzers vapour-deposition apparatus rebuilt by Covion. The unit was likewise fitted with automatic rate and layer-thickness control.

The substances of the mixtures mentioned in the examples are prepared again after the examples.

#### Example 1:

The layer structure corresponded to that described above: glass / ITO / PEDOT / NaphDATA / spiro-TAD / EML = spiro-DPVBi (+ spiro-TAD) / Alq / Ba / Ag. The two materials of the EML (the substances spiro-DPVBi + spiro-TAD) were developed and synthesised by Covion. The EML consisted of a mixture of the two substances (spiro-DPVBi + spiro-TAD), where spiro-TAD had a content of 10%. Furthermore,

OLEDs were produced as reference without the substance spiro-TAD in the EML. In the case of the mixture in the EML, the lifetime of the OLED increased by a factor of 3 compared with the reference OLED; more precisely from about 1500 h to 4500 h. At the same time, the photometric efficiency (unit cd/A) was improved by about 10% and the power efficiency was likewise increased. If a mixture of spiro-TAD and spiro-DPVBi having a concentration of 15% of spiro-DPVBi was prepared, the lifetime increased by a factor of 4; more precisely from about 1500 h to 6000 h. Furthermore, steeper I-U-EL characteristic lines were obtained, i.e. lower voltages were required in order to achieve a certain brightness, for example only 4.5 V instead of 5.5 V for a brightness of 100 cd/m<sup>2</sup>.

#### Example 2:

The layer structure corresponded to that described above: glass / ITO / PEDOT / NaphDATA / spiro-TAD / EML = spiro-DPVBi (+ spiro-AA2) / Alq / Ba / Ag. The two materials of the EML (the substances spiro-DPVBi and spiro-AA2) were developed and synthesised by Covion. The EML consisted of a mixture of the two substances (spiro-DPVBi and spiro-AA2), where spiro-AA2 had a content of 10%. Furthermore, OLEDs were produced as reference without the substance spiro-AA2 in the EML. In the case of the mixture in the EML, the lifetime of the OLED increased by a factor of >8 compared with the reference OLED; more precisely from about 1500 h to >12,000 h. Furthermore, steeper I-U-EL characteristic lines were obtained, i.e. lower voltages were required in order to achieve a certain brightness, for example only 4.5 V instead of 5.5 V for a brightness of 100 cd/m<sup>2</sup>.

#### Example 3:

The layer structure corresponded to that described above: glass / ITO / PEDOT / NaphDATA / spiro-TAD / EML = spiro-Ant1 (+ spiro-TAD) / Alq / Ba / Ag. The two materials of the EML (the substances spiro-Ant1 and spiro-TAD) were developed and synthesised by Covion. The EML consisted of a mixture of the two substances (spiro-Ant1 and spiro-TAD), where spiro-TAD had a content of 50%. Furthermore, OLEDs were produced as reference without the substance spiro-TAD in the EML. In the case of the mixture in the EML, the lifetime of the OLED increased by a factor of >100 compared with the reference OLED; more precisely from about 100 h to

>10,000 h. Furthermore, steeper I-U-EL characteristic lines were obtained, i.e. lower voltages were required in order to achieve a certain brightness, for example only 4.5 V instead of 6 V for a brightness of 100 cd/m<sup>2</sup>.

#### Example 4:

The layer structure corresponded to that described above: glass / ITO / PEDOT / NaphDATA / spiro-TAD / EML = spiro-Ant2 (+ spiro-TAD) / Alq / Ba / Ag. The two materials of the EML (the substances spiro-Ant2 and spiro-TAD) were developed and synthesised by Covion. The EML consisted of a mixture of the two substances (spiro-Ant2 and spiro-TAD), where spiro-TAD had a content of 10%. Furthermore, OLEDs were produced as reference without the substance spiro-TAD in the EML. In the case of the mixture in the EML, the lifetime of the OLED increased by a factor of >3 compared with the reference OLED; more precisely from about 300 h to >900 h. Furthermore, steeper I-U-EL characteristic lines were obtained, i.e. lower voltages were required in order to achieve a certain brightness, for example only 5.5 V instead of 6.5 V for a brightness of 100 cd/m<sup>2</sup>.

#### Example 5:

The layer structure corresponded to that described above: glass / ITO / PEDOT / NaphDATA / spiro-TAD / EML = spiro-pyrene (+ spiro-TAD) / Alq / Ba / Ag. The two materials of the EML (the substances spiro-pyrene and spiro-TAD) were developed and synthesised by Covion. The EML consisted of a mixture of the two substances (spiro-pyrene and spiro-TAD), where spiro-TAD had a content of 10%. Furthermore, OLEDs were produced as reference without the substance spiro-TAD in the EML. In the case of the mixture in the EML, the lifetime of the OLED increased by a factor of 3 compared with the reference OLED; more precisely from about 1500 h to 4500 h. At the same time, the photometric efficiency (unit cd/A) was improved by up to 20% and the power efficiency was likewise increased. Furthermore, steeper I-U-EL characteristic lines were obtained, i.e. lower voltages were required in order to achieve a certain brightness, for example only 4.5 V instead of 5.5 V for a brightness of 100 cd/m<sup>2</sup>.

## Example 6:

The layer structure corresponded to that described above: glass / ITO / PEDOT / NaphDATA / spiro-TAD / EML = TBPP (+ spiro-TAD) / Alq / Ba / Ag. The two materials of the EML (the substances TBPP and spiro-TAD) were developed and synthesised by Covion. The EML consisted of a mixture of the two substances (TBPP and spiro-TAD), where spiro-TAD had a content of 10%. Furthermore, OLEDs were produced as reference without the substance spiro-TAD in the EML. In the case of the mixture in the EML, the lifetime of the OLED increased by a factor of 10 compared with the reference OLED; more precisely from about 500 h to 5000 h. At the same time, the photometric efficiency (unit cd/A) was improved by up to 100% and the power efficiency was likewise increased. Furthermore, steeper I-U-EL characteristic lines were obtained, i.e. lower voltages were required in order to achieve a certain brightness, for example only 6 V instead of 7 V for a brightness of 100 cd/m<sup>2</sup>.

## Example 7:

The layer structure corresponded to that described above: glass / ITO / PEDOT / NaphDATA / spiro-TAD / EML = DTBTD (+ spiro-TAD) / Alq / Ba / Ag. The two materials of the EML (the substances DTBTD and spiro-TAD) were developed and synthesised by Covion. The EML consisted of a mixture of the two substances (DTBTD and spiro-TAD), where spiro-TAD had a content of 10%. Furthermore, OLEDs were produced as reference without the substance spiro-TAD in the EML. In the case of the mixture in the EML, the lifetime of the OLED increased by a factor of 8 compared with the reference OLED; more precisely from about 500 h to 4000 h.

## Example 8:

The layer structure corresponded to that described above: glass / ITO / PEDOT / NaphDATA / spiro-TAD / EML = BDPBTD (+ spiro-TAD) / Alq / Ba / Ag. The two materials of the EML (the substances BDPBTD and spiro-TAD) were developed and synthesised by Covion. The EML consisted of a mixture of the two substances (BDPBTD and spiro-TAD), where spiro-TAD had a content of 90%. Furthermore, OLEDs were produced as reference without the substance spiro-TAD in the EML. In the case of the mixture in the EML, the lifetime of the OLED increased by a factor of >10 compared with the reference OLED; more precisely from about 1000 h to

>10,000 h. At the same time, the photometric efficiency (unit cd/A) was improved by up to 100% and the power efficiency was likewise increased. Furthermore, steeper I-U-EL characteristic lines were obtained, i.e. lower voltages were required in order to achieve a certain brightness, for example only 5 V instead of 8 V for a brightness of 100 cd/m<sup>2</sup>.

#### Example 9:

The layer structure corresponded to that described above: glass / ITO / PEDOT / NaphDATA / spiro-TAD / EML = BDTBTD (+ spiro-TAD) / Alq / Ba / Ag. The two materials of the EML (the substances BDTBTD and spiro-TAD) were developed and synthesised by Covion. The EML consisted of a mixture of the two substances (BDTBTD and spiro-TAD), where spiro-TAD had a content of 90%. Furthermore, OLEDs were produced as reference without the substance spiro-TAD in the EML. In the case of the mixture in the EML, the lifetime of the OLED increased by a factor of 10 compared with the reference OLED; more precisely from about 1000 h to >10,000 h. At the same time, the photometric efficiency (unit cd/A) was improved by up to 400% and the power efficiency was likewise increased. Furthermore, steeper I-U-EL characteristic lines were obtained, i.e. lower voltages were required in order to achieve a certain brightness, for example only 6 V instead of 9 V for a brightness of 100 cd/m<sup>2</sup>.

#### Example 10:

The layer structure corresponded to that described above incorporating the HBL: glass / ITO / PEDOT / NaphDATA / spiro-TAD / EML = IrPPy (+spiro-carbazole) / BCP / Alq / Ba / Ag. The two materials of the EML (the substances IrPPy and spiro-carbazole) were developed and synthesised by Covion. The EML consisted of a mixture of the two substances (IrPPy and spiro-carbazole), where spiro-carbazole had a content of 90%. Furthermore, OLEDs were produced as reference without the substance spiro-carbazole in the EML. The photometric efficiency (unit cd/A) was improved by up to 500% and the power efficiency was likewise increased. Furthermore, steeper I-U-EL characteristic lines were obtained, i.e. lower voltages were required in order to achieve a certain brightness, for example only 6 V instead of 9 V for a brightness of 100 cd/m<sup>2</sup>.

## Example 11:

The layer structure corresponded to that described above incorporating the HBL: glass / ITO / PEDOT / NaphDATA / spiro-TAD / EML = IrPPy (+spiro-4PP6) / BCP / Alq / Ba / Ag. The two materials of the EML (the substances IrPPy and spiro-4PP6) were developed and synthesised by Covion. The EML consisted of a mixture of the two substances (IrPPy and spiro-4PP6), where spiro-4PP6 had a content of 90%. Furthermore, OLEDs were produced as reference without the substance spiro-4PP6 in the EML. The photometric efficiency (unit cd/A) was improved by up to 400% and the power efficiency was likewise increased. Furthermore, steeper I-U-EL characteristic lines were obtained, i.e. lower voltages were required in order to achieve a certain brightness, for example only 5.5 V instead of 9 V for a brightness of 100 cd/m<sup>2</sup>.

## Example 12:

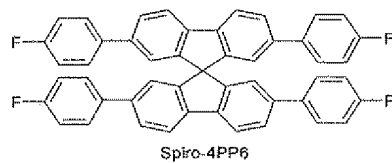
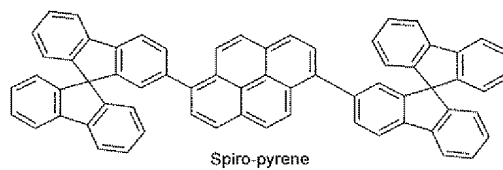
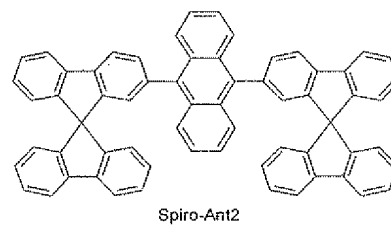
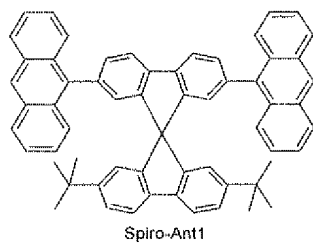
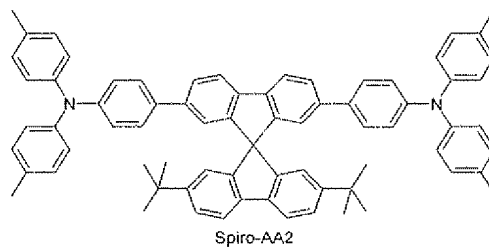
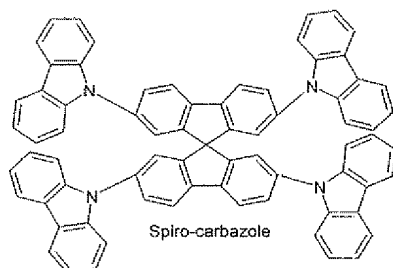
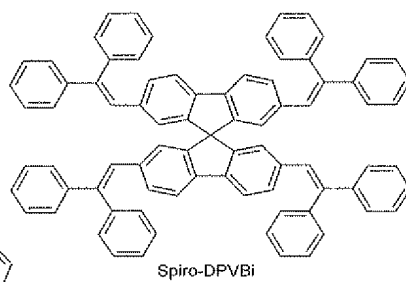
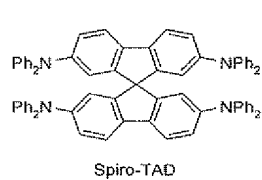
The layer structure corresponded to that described above: glass / ITO / PEDOT / NaphDATA / spiro-TAD / EML = spiro-Ant2 (+CPB) / Alq / Ba / Ag. The two materials of the EML (the substances spiro-Ant2 and CPB) were developed and synthesised by Covion. The EML consisted of a mixture of the two substances (spiro-Ant2 and CPB), where CPB had a content of 20%. Furthermore, OLEDs were produced as reference without the substance CPB in the EML. In the case of the mixture in the EML, the lifetime of the OLED increased by a factor of 6 compared with the reference OLED; more precisely from about 300 h to >1800 h. Furthermore, steeper I-U-EL characteristic lines were obtained, i.e. lower voltages were required in order to achieve a certain brightness, for example only 6 V instead of 7 V for a brightness of 100 cd/m<sup>2</sup>. In addition, the colour coordinates improved, CIE values of  $x = 0.15$  and  $y = 0.15$  were achieved in the reference OLED,  $x = 0.15$  and  $y = 0.12$  were achieved with a proportion of 20% of CPB.

## Example 13:

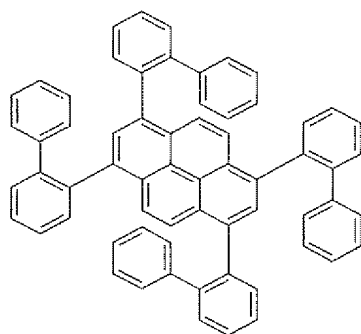
The layer structure corresponded to that described above: glass / ITO / PEDOT / NaphDATA / spiro-TAD / EML = spiro-pyrene (+CPB) / Alq / Ba / Ag. The two materials of the EML (the substances spiro-pyrene and CPB) were developed and

synthesised by Covion. The EML consisted of a mixture of the two substances (spiro-pyrene and CPB), where CPB had a content of 10%. Furthermore, OLEDs were produced as reference without the substance CPB in the EML. In the case of the mixture in the EML, the lifetime of the OLED increased by a factor of 6 compared with the reference OLED; more precisely from about 300 h to >1800 h. Furthermore, steeper I-U-EL characteristic lines were obtained, i.e. lower voltages were required in order to achieve a certain brightness, for example only 6 V instead of 7 V for a brightness of 100 cd/m<sup>2</sup>. In addition, the colour coordinates improved, CIE values of  $x = 0.15$  and  $y = 0.20$  were achieved in the reference OLED,  $x = 0.15$  and  $y = 0.17$  were achieved with a proportion of 10% of CPB.

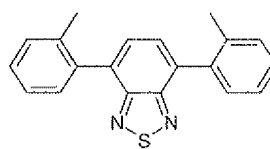
For better clarity, the substances mentioned in the above-mentioned examples are shown again below:



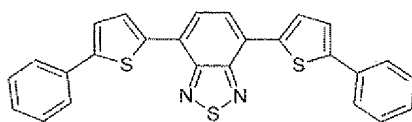




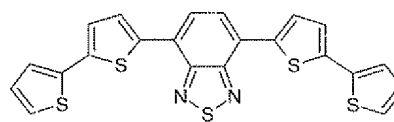
TBPP



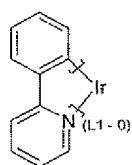
DTBTD



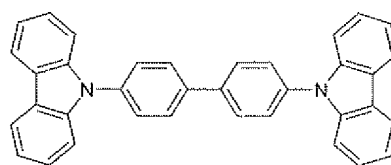
BDPBTD



BDTBTD



IrPPy



CPB

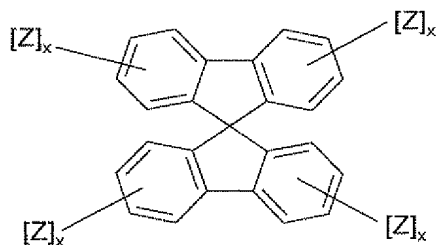
## Patent Claims:

2002/CVG 045

1. Organic electroluminescent device which has at least one emitting layer (EML), where this comprises a mixture of at least one hole-conductor material and at least one emission-capable emission material, and at least one of the two materials contains one or more spiro-9,9'-bifluorene units and the weight ratio of hole-conductor material to emission material is 1 : 99 to 99 : 1, preferably from 5 : 95 to 80 : 20, particularly preferably from 5 : 95 to 25 : 75.
2. Organic electroluminescent device according to Claim 1, characterised in that it has at least one emitting layer (EML), where this comprises a mixture of at least one hole-conductor material and at least one emission-capable emission material, where the HOMO of the hole-conductor material is in the range from 4.8 to 5.8 eV (vs. vacuum), and the compound has at least one substituted or unsubstituted diarylamino group, preferably at least one triarylamino unit or a carbazole group, and the emission-capable emission material contains one or more spiro-9,9'-bifluorene units and the weight ratio of hole-conductor material to emission material is 1 : 99 to 99 : 1, preferably from 5 : 95 to 80 : 20, particularly preferably from 5 : 95 to 25 : 75.
3. Organic electroluminescent device according to Claim 1, characterised in that it has at least one emitting layer (EML), where this comprises a mixture of at least one hole-conductor material and at least one emission-capable emission material, where the HOMO of the hole-conductor material is in the range from 4.8 to 5.8 eV (vs. vacuum), and the compound contains one or more spiro-9,9'-bifluorene units and at least one group selected from substituted or unsubstituted diarylamino, carbazole or thiophene units, and the emission-capable emission material is selected from the group of the metal complexes, stilbenamines, stilbenarylenes, condensed aromatic or heteroaromatic systems, but also phosphorescent heavy-metal complexes, rhodamines, coumarins, substituted or unsubstituted aluminium, zinc, gallium hydroxyquinolinates, bis(p-diarylamino)styryl-arylenes, DPVBi (4,4'-bis(2,2-diphenylvinyl)biphenyl) and analogous compounds, anthracenes, naphthacenes, pentacenes, pyrenes, perylenes, rubrene, QA, benzothiadiazole compounds, DCM (4-(dicyanomethylene)-2-methyl-6-(4-

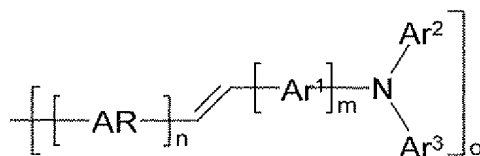
dimethylaminostyryl)-4H-pyran), DCJTB ([2-(1,1-dimethylethyl)-6-[2-(2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H-benzo[ij]quinolizin-9-yl)ethenyl]-4H-pyran-4-ylidene]propanedinitrile), iridium, europium, or platinum complexes, and the weight ratio of hole-conductor material to emission material is 1 : 99 to 99 : 1, preferably from 5 : 95 to 80 : 20, particularly preferably from 5 : 95 to 25 : 75.

4. Organic electroluminescent device according to Claim 1, characterised in that it has at least one emitting layer (EML), where this comprises a mixture of at least one hole-conductor material and at least one emission-capable emission material, where the HOMO of the hole-conductor material is in the range from 4.8 to 5.8 eV (vs. vacuum), and the compound contains one or more spiro-9,9'-bifluorene units and at least one group selected from substituted or unsubstituted diarylamino, carbazole or thiophene units, and the emission-capable emission material contains at least one spiro-9,9'-bifluorene unit and the weight ratio of hole-conductor material to emission material is 1 : 99 to 99 : 1, preferably from 5 : 95 to 80 : 20, particularly preferably from 5 : 95 to 25 : 75.
5. Organic electroluminescent device according to one or more of Claims 1 to 4, characterised in that the glass-transition temperature  $T_g$  of the hole-conductor materials is greater than 90°C.
6. Organic electroluminescent device according to one or more of Claims 1 to 5, characterised in that the glass-transition temperature  $T_g$  of the emission materials is greater than 100°C.
7. Compounds of the formula (I)



Formula (I)

in which the radical Z stands for one or more groups of the formula



in which

AR, Ar<sup>1</sup>, Ar<sup>2</sup> and Ar<sup>3</sup> are on each occurrence, identically or differently, aromatic or heteroaromatic rings having 4 to 40 C atoms, which may be substituted by substituents R<sup>1</sup> at the free positions;

n is on each occurrence, identically or differently, 0, 1, or 2;

m is on each occurrence, identically or differently, 1 or 2;

o is on each occurrence, identically or differently, 1, 2, 3, 4, 5 or 6;

x is on each occurrence, identically or differently, 0, 1, 2, 3 or 4, with the proviso that the sum of all indices x is not equal to zero,

R<sup>1</sup> is on each occurrence, identically or differently, a straight-chain, branched or cyclic alkyl or alkoxy chain having 1 to 22 C atoms, in which, in addition, one or more non-adjacent C atoms may be replaced by N-R<sup>2</sup>, O, S, -CO-O-, O-CO-O-, where, in addition, one or more H atoms may be replaced by fluorine, an aryl or aryloxy group having 5 to 40 C atoms, in which, in addition, one or more C atoms may be replaced by O, S or N, which may also be substituted by one or more non-aromatic radicals R<sup>1</sup>, or Cl, F, CN, N(R<sup>2</sup>)<sub>2</sub>, B(R<sup>2</sup>)<sub>2</sub>, where, in addition, two or more radicals R<sup>1</sup> may form a ring system with one another;

R<sup>2</sup> is on each occurrence, identically or differently, H, a straight-chain, branched or cyclic alkyl chain having 1 to 22 C atoms, in which, in addition, one or more non-adjacent C atoms may be replaced by O, S, -CO-O-, O-CO-O-, where, in addition, one or more H atoms may be replaced by fluorine, an aryl group having 5 to 40 C atoms, in which, in addition, one or

more C atoms may be replaced by O, S or N, which may also be substituted by one or more non-aromatic radicals R<sup>1</sup>.

8. Use of the compounds according to Claim 7 for the production of organic electro-luminescent devices.

## Organic electroluminescent element

5 The present invention relates to the improvement of organic electroluminescent devices, which is characterised in that the emitting layer (EML) consists of a mixture of two substances, where one has hole-conducting properties and the other has light-emitting properties, and at least one of these compounds contains a spiro-9,9'-bifluorene unit.

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